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IDENTIFICATION AND QUANTIFICATION OF NITROPOLYNUCLEAR AROMATIC HYDROCARBONS IN AMBIENT AND INDOOR AIR PARTICULATE SAMPLES

by

Cheng C. Chuang[1], Gregory A. Mack[1], Bruce A. Petersen[1,2], Nancy K. Wilson[3]

[1]Battelle Columbus Laboratories, Columbus, OH 43201

[2]SCIEX, Inc., Worthington, OH 43085

[3]Environmental Monitoring Systems Laboratory, USEPA, Cincinnati, OH 45268

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EPA Project Officer
Nancy K. Wilson

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT

Polynuclear aromatic hydrocarbons (PAH) and nitro-substituted polynuclear aromatic hydrocarbons (NO_2-PAH) have been identified in organic extracts of ambient air particulate matter. Many of the identified PAH and NO_2-PAH are potent carcinogens and/or mutagens. Therefore the determination of PAH and NO_2-PAH in ambient air is of considerable importance to the characterization of air quality. A study was conducted to estimate the influence of PAH and NO_2-PAH concentration in residences as a result of the following parameters: 1) smoking; 2) wood burning fireplaces; 3) home utilities; 4) ambient air intrusion. Eight study homes and two background homes located in Columbus, OH were sampled in March 1984. Test parameters included the presence or absence of smokers, wood burning fire places, and gas or electric utilities. Samples were taken for 24 hours by using a modified EPA/SURC medium volume sampler. A quartz fiber filter was used to collect particulate matter and a polyurethane foam cartridge was used to trap vapors. This presentation will emphasize the analytical methods and the results of the NO_2-PAH determinations from both ambient and indoor air samples. The identification and quantification of NO_2-PAH were accomplished using an on-column injection, negative chemical ionization gas chromatography/mass spectrometry (NCI GC/MS) technique, in the multiple ion detection mode (MID). A statistical analysis of these data was conducted to evaluate the test parameter effects on NO_2-PAH levels.

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IDENTIFICATION AND QUANTIFICATION OF NITROPOLYNUCLEAR AROMATIC HYDROCARBONS IN AMBIENT AND INDOOR AIR PARTICULATE SAMPLES

CHENG C. CHUANG*[1], GREGORY A. MACK[1], BRUCE A. PETERSEN[1,2], NANCY K. WILSON[3]
(1) Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201 (2) SCIEX, Inc., 100 East Wilson Bridge Road, Worthington, Ohio 43085, (3) U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) and nitro-substituted polynuclear aromatic hydrocarbons (NO_2-PAH) have been identified in organic extracts of ambient air particulate matter [1-3]. The presence of PAH in the atmosphere has been thoroughly investigated. However very few studies involved the determination of NO_2-PAH in air particulate matter. Many of the identified PAH and NO_2-PAH are potent carcinogens and/or mutagens[3-5]. Therefore, the determination of PAH and NO_2-PAH in air is of considerable importance to the characterization of air quality.

A study was conducted to develop, evaluate and test a generic sampling and analysis methodology to characterize PAH and NO_2-PAH concentrations in ambient and indoor air. As a part of this study, the influences on the range of PAH and NO_2-PAH concentrations in air within residences were estimated as functions of the following factors:

- cigarette smoking
- wood burning fireplaces
- home utilities

This study involved sampling PAH and NO_2-PAH levels at ten different residences in Columbus, Ohio. Two of the residences were used as controls and the remaining eight were selected according to specific characteristics. The types of residences that were selected are:

(1) Two control homes with

- all electric appliances and heating system
- no cigarette smokers present
- no wood burning fireplaces in use during the survey.

(2) Eight experimental homes with

- all gas appliances and heating system
- various combinations of conditions with respect to cigarette smoking and wood burning fireplaces

The indoor and ambient samples were collected using quartz fiber filters and polyurethane foam (PUF) backup traps. These samples were analyzed by gas chromatography/mass spectrometry (GC/MS) for the determination of PAH, nitrogen heterocycles, and NO_2-PAH.

This paper presents only the data from the NO_2-PAH determinations. The PAH data will be presented at a later date.

MATERIAL AND METHODS

Sampling

The indoor air samples were collected over eight hours at three different locations in the homes--the kitchen, living room and bedroom. A modified EPA medium volume sampler using a rotary carbon vane oil-less vacuum pump was employed. The dual chamber sampling module consisted of a quartz fiber filter and PUF cartridge to collect particulate matter and vapors, respectively. The pumping unit was located outside the house. A flexible hose connecting the sampling module to the pumping station was passed through an open window. The opening was then sealed with one-inch thick extruded polystyrene insulation. A 24-hour outdoor ambient air sample was collected at each residential site with an EPA medium volume sampler[6]. Sampling locations were selected to avoid interferences from exhaust openings or flue vents in the house. The air exchange rate of each house was determined from the gas chromatography/electron capture detection (GC/ECD) time profile of injected sulfur hexafluoride (SF_6). The sampling conditions are summarized in Tables 1 and 2.

TABLE 1

SUMMARY OF THE SAMPLING CONDITIONS FOR ELECTRIC HEATED HOMES

MATRIX OF ELECTRIC-HEATED HOMES TESTED (Control Homes)

	NO FIREPLACE IN USE	
		Sampling Date
NO SMOKING	Home G	3/21/84
	Home H	3/21/84

TABLE 2

SUMMARY OF THE SAMPLING CONDITIONS FOR GAS HEATED HOMES

MATRIX OF GAS-HEATED HOMES TESTED

	NO FIREPLACE IN USE		FIREPLACE USED	
		Sampling Date		Sampling Date
NO SMOKING	Home A	3/12/84	Home B	3/13/84
	Home I	3/23/84	Home C	3/13/84
			Home C2	3/27/84
SMOKING	Home E	3/19/84	Home D	3/14/84
	Home J	3/27/84	Home F	3/19/84
			Home F2	3/27/84

Extraction of Filter and PUF Samples

Soluble organic material was removed from the filter and PUF cartridge by Soxhlet extraction with methylene chloride and 5% ethyl ether/hexane respectively. Extractions were carried out until the solvents in the Soxhlet extractor top chamber became colorless or for at least 16 hours. The extracts were concentrated by Kuderna-Danish (K-D) evaporation to a final volume of 1 ml for GC/MS analysis.

Negative Chemical Ionization, Gas Chromatography/Mass Spectrometry (NCI GC/MS) Method

The determination of NO_2-PAH was accomplished using an on-column injection NCI GC/MS technique in the multiple ion detection mode (MID). The instrumental conditions used are listed in Table 3. A Finnigan Model 4500 quadrupole mass spectrometer equipped with an EI/CI source was used. Methane was used as the reagent gas with a source pressure of 1.0 torr, and was ionized by a 200 eV electron beam. Data acquisition and processing were performed with a Finnigan INCOS model 2100 data system.

Gas chromatography employed an Ultra #2 fused silica capillary column (50 m x 0.31 mm ID, 0.17 µm film thickness, Hewlett Packard Co.) and methane carrier gas. The GC column was interfaced directly to the MS ion source. With the on-column injection technique, the sample was injected at 45°C to prevent thermal degradation of NO_2-PAH. The GC column temperature was held at 45°C for 2 min, programmed ballistically to 100°C in 5 min, and then programmed from 100°C to 320°C at 10°C/min.

The ion peaks monitored by the MS were the molecular ion peaks $(M)^-$ and the fragment ion peaks $(M-30)^-$ of the compounds of interest. The quantifications of NO_2-PAH were accomplished by comparison of their respective integrated ion current responses to that of the D_9-nitropyrene chromatographic internal standard, and interpolation on standard curves. The standard response curve included measurements at three levels (0.1 ng/µl, 0.01 ng/µl and 0.001 ng/µl). Full mass scan analyses of three sample extracts were conducted and the results were used for confirmation of the identifications from the MID technique.

TABLE 3

GC AND MS OPERATING CONDITIONS

Chromatography	
Column:	HP Ultra #2 crosslinked 5% phenyl methyl silicon 50 m x 0.31 mm, 0.17 μm film thickness
Carrier:	methane
Carrier linear flow velocity:	50 cm/sec. at 250°C
Injection volume:	1 μl
Injection mode:	on-column
Temperature Program	
Initial column temperature:	45°C
Initial hold time:	2 minutes
Program rate:	100°C (5 minutes) to 320°C at 10°C/min.
Final hold time:	10 minutes
Mass Spectrometer	
Reagent gas:	methane
Ionization:	NCI at 200 ev
Filament emission current:	0.3 m amp
Preamplifier:	10^{-8} amp/volt
Electron multiplier gain:	$\sim 10^5$ gain
Ion source temperature:	180°C

RESULTS AND DISCUSSION

Both 1-nitropyrene and 3-nitrofluoranthene were identified and quantified in the extracts of indoor and outdoor air particulate matter. The levels of these compounds were much lower than levels of their parent compounds, pyrene and fluoranthene. Neither dinitropyrene nor dinitrofluoranthene isomers were detected in these sample extracts. Quantities of the detected NO_2-PAHs are listed in Table 4. A typical chromatogram from the NCI GC/MS analysis of a sample extract is shown in Figure 1.

The on-column injection NCI GC/MS technique in the full scan mode has been demonstrated, in several studies conducted at Battelle[3,7,8], to be a sensitive and selective method for the determination of NO_2-PAHs. In this study, the mass spectrometer was operated in the multiple ion detection (MID) mode. In the MID mode, the mass spectrometer sequentially monitors one or more ion peaks characteristic of a specific compound, during its expected elution time from the gas chromatographic column. Because the ion peaks monitored are specific to the NO_2-PAH compounds being analyzed, ion peaks from other compounds at non-monitored masses do not contribute to the monitored ion current signal. Therefore other compounds do not interfere with the analysis. The MID mode enhances the sensitivity by approximately two orders of magnitude over the full scan mode. The advantage of using this method is that sample clean-up steps are not required for the determination of NO_2-PAH in air particulate extracts. The total sample preparation time and cost can thus be significantly decreased. However, as shown in Table 4 there were coeluting interferences with the NO_2-PAH peaks in three of the sample extracts. It should be noted that these three filter samples were highly loaded with particulate material and contained higher levels of extractable organic material than that of a typical filter sample. These interferences can be resolved by using a silica gel column chromatography clean-up method.[9]

Data for the NO_2-PAH indicated that 3-nitrofluoranthene was present at a higher concentration level than 1-nitropyrene for all the samples except for home A. The relatively higher levels of 1-nitropyrene compared to 3-nitrofluoranthene in home A may have resulted from

TABLE 4

NITRO-PAH CONCENTRATION IN AIR SAMPLED FROM STUDY HOMES AND BACKGROUND HOMES

		CONCENTRATION - ng/m^3	
Home Code	Location Code	1-Nitropyrene	3-Nitrofluoranthene
A	I (1)	0.069	0.032
A	O (2)	0.025	0.082
B	I	0.026	0.030
B	O	0.038	0.086
C	I	0.019	0.028
C	O	0.042	0.049
C2	I	0.026	0.061
C2	O	0.019	0.185
D	I	0.056	0.087
D	O	0.020	0.028
E	I	0.052	0.143
E	O	0.013	0.120
F	I	0.014	0.071
F	O	0.027	0.167
F2	I	0.005	0.055
F2	O	0.017	0.161
G	I	0.003	0.008
G	O	0.003	0.005
H	I	0.004	0.067 (3)
H	O	0.002	0.006
I	I	0.010	0.013
I	O	0.038	0.052
J	I	INT(3)	0.134 (3)
J	O	0.047	0.168

(1) I = Indoor filter and PUF at three locations, combined samples.

(2) O = Outdoor filter and PUF combined samples

(3) INT = Interference peak coeluted with target compound.

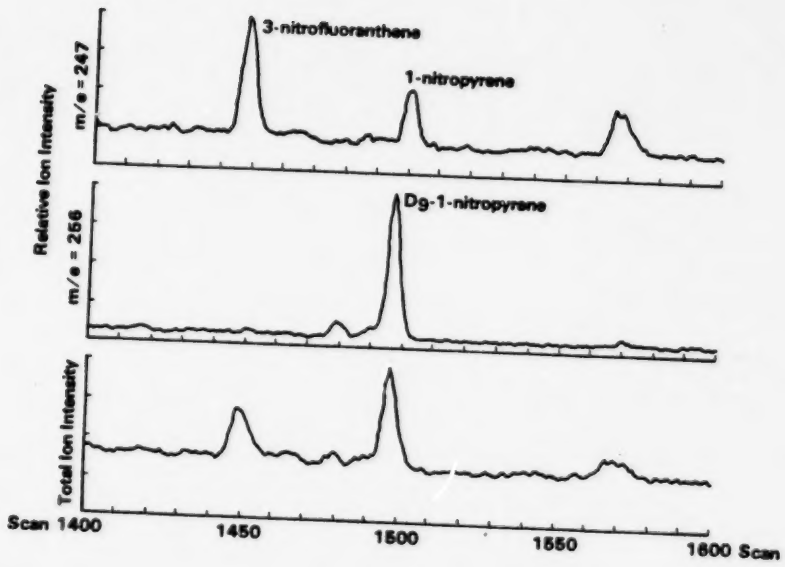

FIGURE 1. Multiple ion detection chromatogram of 3-nitrofluoranthene and 1-nitropyrene in the extract of an air particulate sample.

contamination by a local mobile source during sampling. In mobile source emission samples, 1-nitropyrene was detected at higher concentrations than 3-nitrofluoranthene(7-8). Similarly, the ambient air samples that were heavily influenced by mobile source emission, also had the same comparative concentration levels of 1-nitropyrene and 3-nitrofluoranthene(3). The remaining samples were not significantly influenced by mobile source emissions. Therefore, as shown in Table 3, these samples contained levels of 3-nitrofluoranthene greater than 1-nitropyrene.

A statistical analysis of NO_2-PAH data was employed to assess the relationships between the test parameters and the observed NO_2-PAH concentration levels. Summary statistics were generated to compare the observed NO_2-PAH concentration levels between homes having different experimental conditions. For example, homes having woodburning fireplaces in use were compared to homes not having fireplaces. The summary statistics included average concentration levels, standard deviations, minimums, and maximums. The specific comparisons that were made are as follows:

- Homes having woodburning fireplaces in use versus those not having fireplaces in use;
- Homes having cigarette smokers present versus those not having smokers;
- Homes having gas heat and appliances versus those having electric; and
- Homes having different characteristics with respect to all three experimental factors (fireplace, smoking, type of heat and appliances.)

These comparisons are illustrated in Figure 2. The results of these comparisons are reported in Tables 5 and 6 and are summarized as follows:

- There was no significant difference between homes having woodburning fireplaces in use and those not having fireplaces;
- The gas homes had significantly higher levels than the electric homes; and

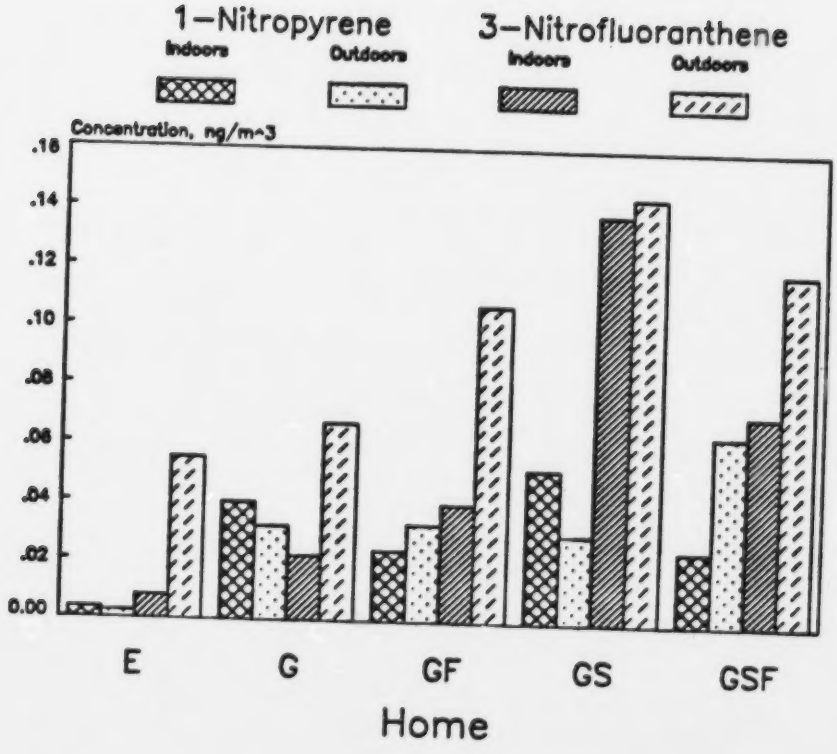

FIGURE 2. Nitro-PAH concentrations, means of combined samples. Type of home: E, electric; G, gas; GF, gas with fireplace; GS, gas with smokers; GSF, gas with fireplace and smokers.

TABLE 5

SUMMARY OF 1-NITROPYRENE CONCENTRATION LEVELS (ng/m^3) FOR THE DIFFERENT COMBINATIONS OF EXPERIMENTAL CONDITIONS

HEATING SYSTEM: GAS

LOCATION	WOOD BURNING	SMOKING	1-NITROPYRENE MEAN	STD	N	MIN	MAX
INDOOR	NO	NO	0.040	0.041	2	0.011	0.069
		YES	0.053		1	0.053	0.053
	YES	NO	0.024	0.004	3	0.019	0.026
		YES	0.025	0.027	3	0.005	0.056
OUTDOOR	NO	NO	0.031	0.009	2	0.025	0.038
		YES	0.030	0.025	2	0.013	0.048
	YES	NO	0.033	0.012	3	0.019	0.042
		YES	0.021	0.005	3	0.017	0.027

TABLE 5 (CONTINUED)

SUMMARY OF 1-NITROPYRENE CONCENTRATION LEVELS (ng/m^3) FOR THE DIFFERENT COMBINATIONS OF EXPERIMENTAL CONDITIONS

HEATING SYSTEM: ELECTRIC

LOCATION	WOOD BURNING	SMOKING	1-NITROPYRENE MEAN	STD	N	MIN	MAX
INDOOR	NO	NO	0.003	0.001	2	0.003	0.004
OUTDOOR	NO	NO	0.002	0.000	2	0.002	0.003

TABLE 6

SUMMARY OF 3-NITROFLUORANTHENE CONCENTRATION LEVELS (ng/m^3) FOR THE DIFFERENT COMBINATIONS OF EXPERIMENTAL CONDITIONS

HEATING SYSTEM: GAS

			3-NITROFLUORANTHENE				
LOCATION	WOOD BURNING	SMOKING	MEAN	STD	N	MIN	MAX
INDOOR	NO	NO	0.023	0.014	2	0.013	0.032
		YES	0.138	0.006	2	0.134	0.143
	YES	NO	0.040	0.019	3	0.028	0.062
		YES	0.071	0.016	3	0.055	0.087
OUTDOOR	NO	NO	0.067	0.021	2	0.052	0.082
		YES	0.144	0.034	2	0.120	0.168
	YES	NO	0.107	0.071	3	0.049	0.185
		YES	0.118	0.078	3	0.028	0.167

TABLE 6 (CONTINUED)

SUMMARY OF 3-NITROFLUORANTHENE CONCENTRATION LEVELS (ng/m^3) FOR THE DIFFERENT COMBINATIONS OF EXPERIMENTAL CONDITIONS

HEATING SYSTEM: ELECTRIC							
			3-NITROFLUORANTHENE				
LOCATION	WOOD BURNING	SMOKING	MEAN	STD	N	MIN	MAX
INDOOR	NO	NO	0.037	0.042	2	0.008	0.067
OUTDOOR	NO	NO	0.005	0.001	2	0.005	0.006

- The effect of cigarette smoking was much more apparent when only those homes having wood burning fireplaces in use were compared among themselves, and when only those homes not having fireplaces were compared.

CONCLUSIONS

The on-column injection NCI GC/MS technique in the MID mode has been demonstrated to be a sensitive and selective method for the analysis of NO_2-PAH in indoor and ambient air samples. It can be used to measure NO_2-PAH in ambient air at concentrations as low as 0.002 ng/m^3 without sample cleanup.

The higher concentration levels of 3-nitrofluoranthene observed in the air particulate samples compared to the levels of 1-nitropyrene suggest that 3-nitrofluoranthene is either more stable than 1-nitropyrene, or that it is more easily formed through atmospheric transformation reactions. In at least one bacterial mutagenesis tester strain (TA98, -S9), 3-nitrofluoranthene elicited a mutagenic response 25 times greater than that of 1-nitropyrene.[10] Considering the relative concentration levels and the relative mutagenicity levels, 3-nitrofluoranthene may be the more significant nitro-PAH for monitoring in ambient air.

The results of the summary statistics indicate that type of heat and appliances and the presence/absence of cigarette smoking were the two most important factors. The presence/absence of wood burning fireplaces did not appear to be significant. In fact, homes having fireplaces had lower observed values for the compounds of interest, although the difference was not statistically significant.

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